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POLYMERIZATION OF N(p-PHENOXY-PHENYL)-METHACRYLAMIDE AND COPOLYMERIZATION WITH STYRENE

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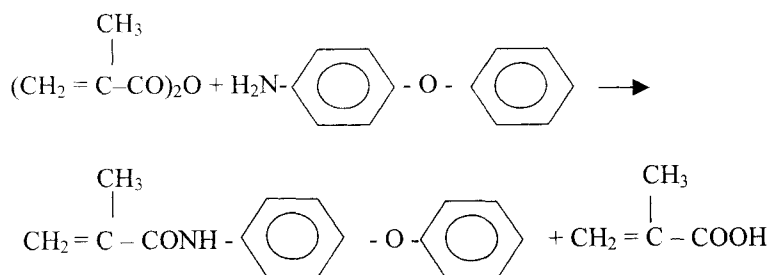
Key Words: PhOPhMAA, poly-PhOPhMAA, poly(PhOPhMAA-co-St),
Reactivity Ratios, Activation Energy, Mechanism of Copolymerization

ABSTRACT

N(p-Phenoxy-phenyl)methacrylamide (PhOPhMAA) prepared by condensation of methacrylic acid anhydride with p-phenoxy-phenylamine readily homopolymerizes and copolymerizes with styrene (St) in the presence of azobisisobutyronitrile as initiator. The copolymers prepared under different monomer-to-monomer ratios in the feed have random composition with an azeotropic point at ratio of 0.65 (St) to 0.35 (PhOPhMAA). Reactivity ratios determined by Kelen-Tüdös method are $r_1(\text{St}) = 0.61$; $r_2(\text{PhOPhMAA}) = 0.55$. Activation energy determined by Arrhenius method is 71.2 kJ mol^{-1} . Poly-PhOPhMAA and poly(PhOPhMAA-co-St) are thermally stable up to 350°C under TGA conditions. T_{gs} and higher transition temperatures are within the thermally stable region.

INTRODUCTION

In a recently published paper, we have described the preparation of N(p-phenoxy-phenyl)maleimide (PhOPhMI), homopolymer poly-PhOPhMI and alternating copolymers with α -methylstyrene, β -methylstyrene and styrene (St) [1]. In



Scheme 1. Synthesis of N(p-phenoxy-phenyl)methacrylamide.

continuation of this work, in the present paper is described the preparation of N(p-phenoxy-phenyl)methacrylamide (PhOPhMAA) (Scheme 1) which was homopolymerized and copolymerized with St by free radical initiated copolymerization in toluene. PhOPhMAA and poly-PhOPhMAA are prepared following the procedure described by Shono and coworkers for the preparation of methacrylamido-benzo-15-crown-5 [2] and poly(methacrylamido-benzo-15-crown-5) [3]. Poly-PhOPhMAA and poly-PhOPhMI belong to the comb-like polymers which, due to the presence of mesogenic groups in side chains, show the tendency to smectic ordering in amorphous matrix. Poly-PhOPhMI and poly-PhOPhMAA have the same mesogenic group in the side chain, but differ significantly in the flexibility of the main chain. It is, therefore, of interest to compare the polymerization conditions and properties of homopolymers and copolymers of N-substituted poly-methacrylamides and poly-maleimides, respectively. Polymerization reactions are performed up to high conversion at equimolar ratios of comonomers and at low conversion at different monomer-to-monomer ratios in feed.

EXPERIMENTAL

Chemicals

p-Phenoxy-phenylamine, Fluka Chemika-Biochemika, pract., > 95%; methacrylic anhydride, Fluka Chemika-Biochemika, pract., ~ 94%.

Synthesis of N(p-Phenoxy-phenyl)methacrylamide

To a solution of 18.5 g (0.1 mol) of p-phenoxy-phenylamine in 160 mL of ether cooled to 10°C, was gradually added under cooling 15.4 g (14.9 mL; 0.1 mol) of methacrylic acid anhydride and the dark solution was left overnight at room

TABLE 1. Polymerization Condition and Properties of Poly-PhOPhMAA and Poly[PhOPhMAA-co-St] in Toluene at a Total Comonomer Concentration of 2 mol L⁻¹ at 70°C with 0.5 wt% of AIBN.

Molar fraction of St in feed	Time		Conv. %	Yield gr	N %	T _g °C	T _{trans} °C	Weight loss /%			
	in copolym. b)	min c)						300°C	350°C	460°C	
0	-	-	60	34	0.1721	5.53	158	345	1.5	6.5	65.5 ^{a)}
0.3	0.35	0.34	85	15.54	0.0648	4.50	144	331	2.7	8.3	90.0
0.4	0.39	0.39	150	19.07	0.0738	4.22	141	329	1.5	7.2	94.9
0.5	0.52	0.52	160	19.11	0.0683	3.82	137	322	3.1	5.3	99.9
0.6	0.58	0.58	190	17.43	0.0570	3.57	134	318	1.0	4.8	100
0.7	0.67	0.68	210	15.36	0.0452	3.03	130	308	1.2	4.5	100
0.8	0.76	0.77	270	8.36	0.0226	2.32	122	304	2.4	5.9	100

a) 98.2% at 480°C; b) based on nitrogen content c) based on ¹H NMR data

temperature. The reaction mixture was extracted with three-60 mL portions of cold 2N-NaOH, washed with water following by the evaporation of ether. The crude amide (25.1 g) was dissolved in 80 mL of chloroform and gradually precipitated under stirring with 500 mL of petrolether (b.p. 40-70°C) yielding 11.8 g (48%) of white crystalline product m.p. 85-90°C. Pure amide was obtained by recrystallization from 20 mL of chloroform and 100 mL of petrolether; yield 10 g (39.4%) m.p. 94-95°C.

Analysis: Calcd. for C₁₆H₁₅NO₂ (253.3): C, 75.89; H, 5.93; N, 5.53. Found: C, 75.69; H, 5.96; N, 5.54.

Polymerization Procedure

Polymerization was performed in 10 mL glass vials thoroughly degassed, filled with nitrogen before sealing and placed into a thermostated oil bath. Polymerization reactions are performed up to high conversion at equimolar ratio of comonomers and at low conversion at different monomer-to-monomer ratios in feed. All polymerizations are performed in toluene at a total monomer concentration of 2 mol L⁻¹ and were initiated with 0.5 wt% of AIBN. The viscous solution of polymers was diluted with chloroform and precipitated by dropwise addition of methanol. The polymer was filtered off and dried in vacuum at 80°C overnight. Composition of copolymer was determined from the nitrogen content (Table 1).

Physicochemical Measurements

NMR spectra were obtained on a Varian EM 390 spectrometer. The copolymer composition was determined by NMR spectroscopy in deuterated dimethylsulfoxide as solvent and by elemental analysis. Molecular weights were determined on a Varian HPGPC Model 5800 using a set of 4 Styrogel columns with THF as solvent. The average molecular weights were calculated by calibrations with standard polystyrenes of known molecular weights. Differential scanning calorimetry was carried out on a Perkin-Elmer model DSC-2 with a scanning rate of 20°C/min in nitrogen with a sample size of 15 mg. Glass transition temperature T_g was taken as the temperature at which the midpoint of the heat capacity change at transition was achieved. The thermogravimetric analysis was carried out on a Perkin-Elmer TGS-2 Thermogravimetric System in a nitrogen stream with a heating rate of 10°C/min.

RESULTS AND DISCUSSION

N(p-Phenoxy-phenyl)methacrylamide was prepared by condensation of methacrylic acid anhydride with p-phenoxy-phenylamine in ether at room temperature. It is of interest to note that if ether is removed from the reaction mixture prior to the extraction of methacrylic acid, the polymer which forms prevents the separation of PhOPhMAA. In contrast to the copolymerization of PhOPhMI with St [1], which forms alternating copolymer, the copolymerization of PhOPhMAA with St is a statistical copolymerization with azeotropic composition of St to PhOPhMAA at a molar ratio of 0.65 to 0.35. The experimental data are summarized in Table 1 and in Figure 1. The copolymerization composition is determined from the nitrogen content in copolymer. The same data were obtained from the NMR spectroscopy.

The reactivity ratios in the copolymerization were determined graphically with the Kelen-Tüdös equation (1) (Figure 2):

$$\eta = r_1\xi - r_2/\alpha \quad (1)$$

where η and ξ are functions of the molar fractions of monomer in the copolymer and in the feed respectively, and α is an arbitrary parameter [4]. Numerical values of the reactivity ratios determined from the Figure 2, using the least-square method, are $r_1(\text{St}) = 0.61$ and $r_2(\text{PhOPhMAA}) = 0.55$.

It was further found that in the copolymerization of PhOPhMAA with St in the presence of 0.3, 0.4 and 0.5 wt% of AIBN, the initial rate of copolymerization is

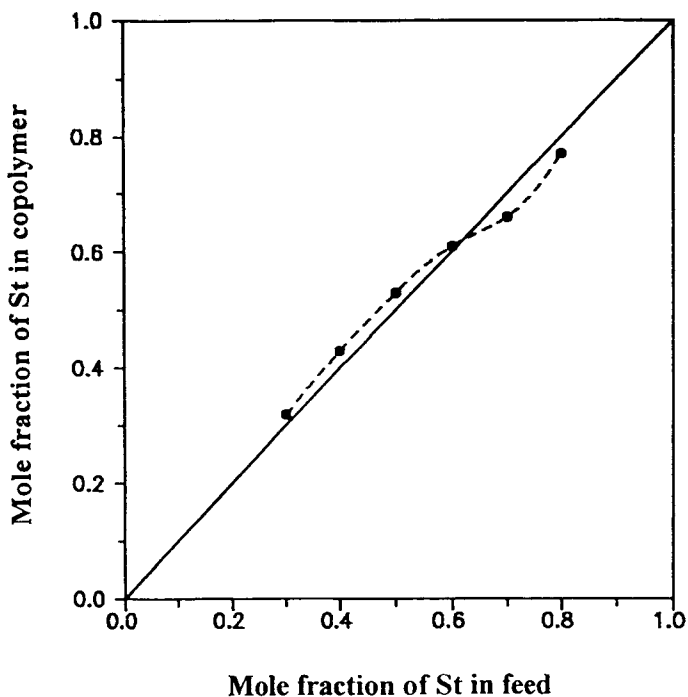


Figure 1. Ratio of molar fraction of St in feed and in copolymer with PhOPhMAA.

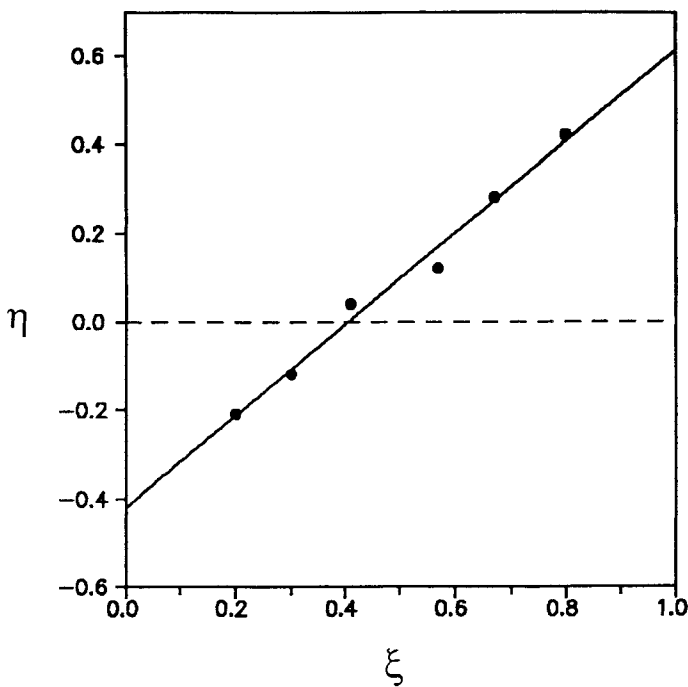


Figure 2. Kelen-Tüdös diagram for calculation of r_1 (St) = 0.61 and r_2 (PhOPhMAA) = 0.55; $\alpha = 1.32$.

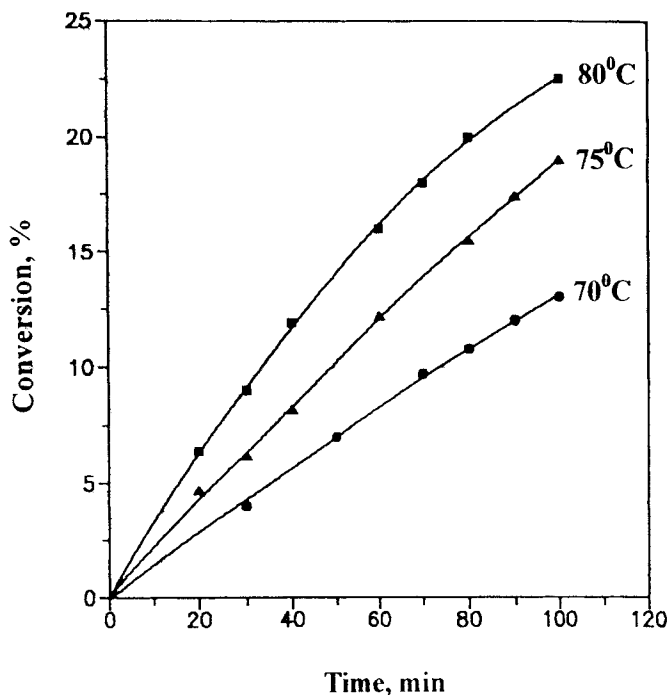


Figure 3. Time-conversion curves in the copolymerization of PhOPhMAA with St in toluene; 0.5 wt% AIBN.

proportional to the square root of AIBN concentration, thus indicating bimolecular termination.

Time-conversion curves in the copolymerization of PhOPhMAA with St at different temperatures at equimolar ratio of comonomers in feed are shown in Figure 3. The linear relationship in the plot of logarithm of initial monomer concentration over the monomer concentration at time t , against time, indicates that the studied copolymerization is a first order reaction in PhOPhMAA as shown in Figure 4. Rate constants of the copolymerization at 70, 75, and 80°C, respectively, are determined as slopes of the straight lines in Figure 4: $k_{70}=0.001404 \text{ min}^{-1}$, $k_{75}=0.002071 \text{ min}^{-1}$, $k_{80}=0.00283 \text{ min}^{-1}$. The activation energy was calculated by graphical method using the Arrhenius equation: $E_A=(\tan\alpha).R/0.4343$, where E_A is the activation energy, $\tan\alpha$ is the slope of straight line from the plot of the logarithm of rate constants against the reciprocal absolute temperature of polymerization, and R is the gas constant. The energy of activation was $71.24 \text{ kJ mol}^{-1}$.

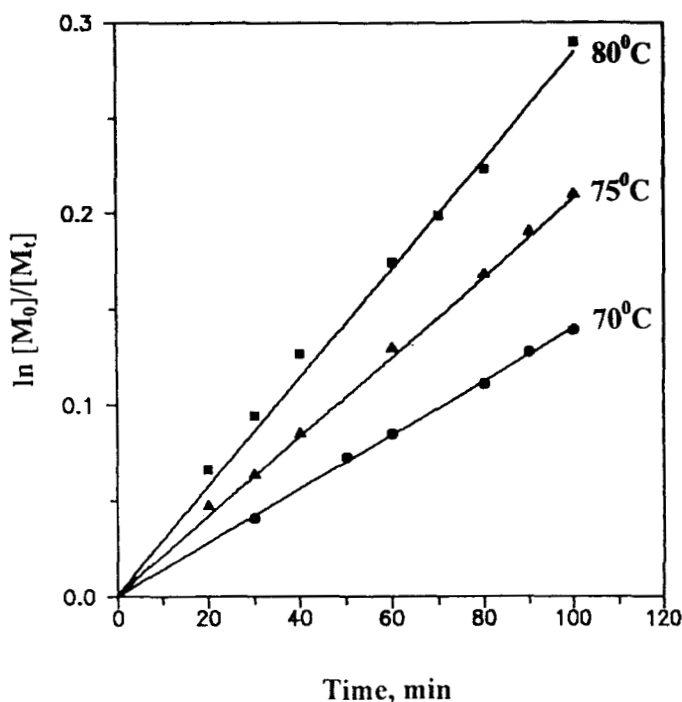


Figure 4. First-order rate plots of the copolymerization of PhOPhMAA with St in toluene at 70°C, 75°C, and 80°C; 0.5 wt% AIBN.

One of the objectives of the present paper is the comparison of the properties of homopolymers poly-PhOPhMAA and poly-PhOPhMI and copolymers with St. It is of interest to note that in repeated experiments PhOPhMAA did not copolymerize under the same experimental conditions with α -MeSt, while N-substituted maleimides readily copolymerize with α -MeSt yielding alternating copolymers [1, 5]. Figures 5 and 6 show that the rate of homopolymerization and copolymerization of PhOPhMAA is much slower than that of PhOPhMI. However molecular weight of poly-PhOPhMAA (M_w 163 700) is much higher than that of poly-PhOPhMI (M_w 31 000) [1]. The opposite was found for copolymers with St prepared at equimolar ratio of comonomers in feed: poly(PhOPhMAA-co-St), M_w =90 300; poly-(PhOPhMI-co-St), M_w =290 000. T_{gS} and T_{trans} of homopolymers and copolymers of PhOPhMAA and PhOPhMI in mesophase are shown in Figure 7. As expected, the T_g of poly-PhOPhMAA which has a value of 158°C is much lower than T_g of rigid poly-PhOPhMI, which has T_g =321°C [1].

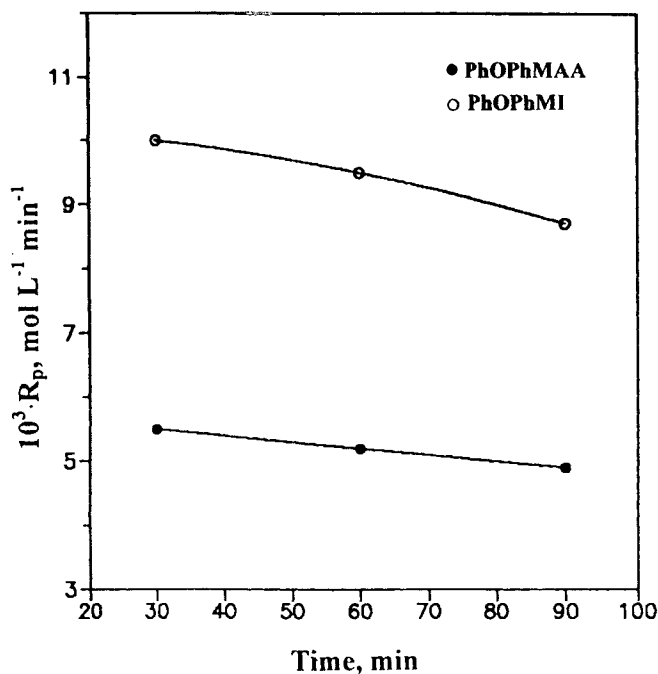


Figure 5. Relationship between rates of polymerization and time in polymerization of PhOPhMAA and PhOPhMI in toluene at 70°C; 0.5 wt% AIBN.

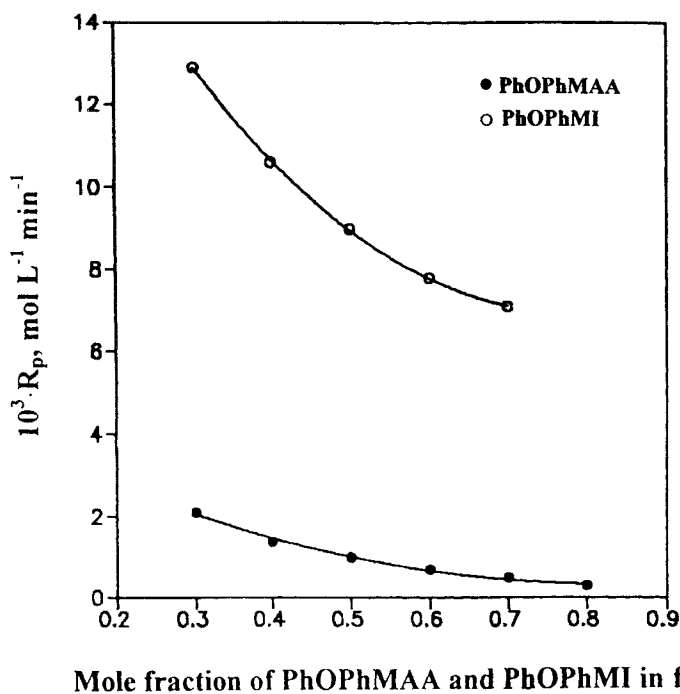


Figure 6. Rates of copolymerization of PhOPhMAA and PhOPhMI with St against molar fraction of monomers in feed in toluene at 70°C; 0.5 wt% AIBN.

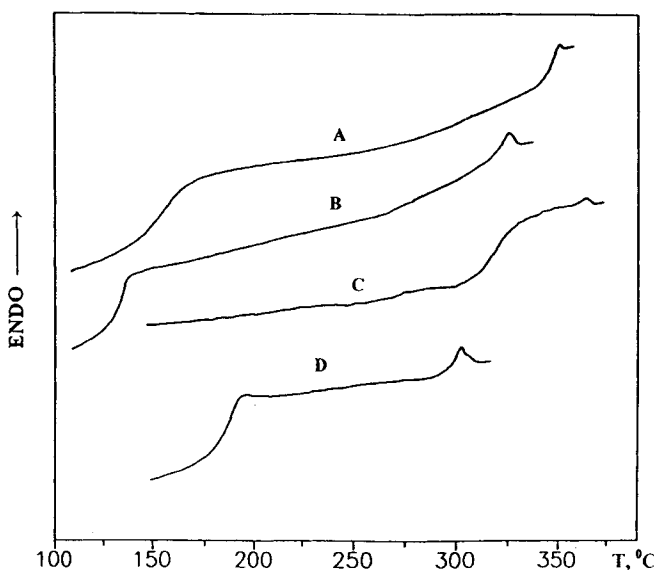


Figure 7. DSC tracings of A) poly-PhOPhMAA; B) poly(PhOPhMAA-co-St); C) poly-PhOPhMI (1); D) poly(PhOPhMI-co-St) (1); scanning rate $20^{\circ}\text{C min}^{-1}$ in N_2 ; second scan.

Copolymerization with St slightly lowers the T_g of N-substituted methacrylamide ($T_g=137^{\circ}\text{C}$) but significantly lowers T_g of poly(PhOPhMI-co-St) ($T_g=190^{\circ}\text{C}$) [1]. Higher transition temperature, T_{trans} , for homopolymers and copolymers in Figure 7 have relatively high values, but in all cases within the thermally stable region.

It is further evident that the region of mesophase is much larger in the homopolymer and copolymer of PhOPhMAA than in the homopolymer and copolymer of PhOPhMI, thus indicating that PhOPhMAA homopolymers and copolymers with St have a higher capability to form regular structure in mesophase than the corresponding maleimido derivatives.

CONCLUSION

N(p-Phenoxy-phenyl)methacrylamide (PhOPhMAA) was prepared by condensation of methacrylic acid anhydride with p-phenoxy-phenylamine in ether at room temperature.

Homopolymerization of PhOPhMAA and copolymerization with St was performed in toluene in the presence of AIBN, and it was found that the copoly-

erization is a statistical reaction with azeotropic composition of St to PhOPhMAA at a molar ratio of 0.65 to 0.35.

From the rate constants of copolymerization at 70, 75 and 80°C the energy of activation was determined by graphical method using the Arrhenius equation. The energy of activation was 71.33 kJ mol⁻¹.

T_g of poly-PhOPhMAA is at 158°C and T_g of poly(PhOPhMAA-co-St) has a value of 137°C. The higher transitions in mesophase are 345°C for homopolymer and 322°C for copolymer prepared at equimolar ratio of comonomers in feed. T_gs and higher transition temperatures are within the thermally stable region.

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